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Interactive comment on “Oxidation photochemistry in the Southern Atlantic boundary layer: unexpected deviations of photochemical steady state” by Z. Hosaynali Beygi et al.

Anonymous Referee #1

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General remarks:

The paper discusses deviations from the photostationary state between NO and NO₂ in clean maritime air from measurements made during a ship cruise on the Southern Atlantic. The deviations are investigated in terms of oxidants other than O₃ and RO₂ that potentially convert NO to NO₂. Model calculations constrained by the data suggest that halogen compounds might play a role in the conversion. The topic of the paper is important for atmospheric photochemistry. However, I cannot recommend publication in ACP before the comments below have been answered successfully.

Major Comments:

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1. I urge the authors to include the NO, NO₂, and O₃ data in Figure 8 prior to publication. (rather than showing individual days in the supplement).

2. The authors argue the small correction for NO losses and corresponding NO₂ production in the inlet line based on gas phase kinetics. However, I miss a thorough discussion of potential NO conversion on the surface of the inlet line, which might be coated with sea salt. In fact, the NO loss/NO₂ production required to explain the deviations from PSS are extremely small in absolute terms! Further, production of NO₂ on surfaces might also contribute to the observed deviations. Did the observed NO₂ artefact exhibit any dependence on, e.g. time of day/JNO₂ or NO₂ or history? Was there a tendency of the fake NO₂ signal to decay if zero air was applied for longer periods? The stated flow rates for the zero air generator are inconsistent with the statement made otherwise in the manuscript about calibrations being performed upstream and downstream of the inlet line. As the determination of potential NO losses is one of the crucial points for the validity of the results, the procedures for calibration and zero air addition must be more clearly described, e.g., how and how often calibrations were performed upstream and downstream of the main inlet line. Furthermore, NO losses or oxidation on the surface of the inlet line may be dependent on the actual NO concentration. It is therefore important to know if the calibration was made at high concentrations or close to those observed in ambient air.

3. I disagree with the statement that the deviation from PSS correlates with JON₂. From Fig 5, the clearest correlation is with NO₂, which may indeed point to artefacts as a potential cause. It may help to expand the discussion on the comparison between so-called pristine air and the few pollution events encountered during the cruise. This discussion would have to include potential differences in the experimental setup (e.g., history of the inlet and instruments, cleaning cycles, etc.)

4. A scatter plot of the RO₂+HO₂ mixing ratio required to explain the deviation from Leighton's ratio (neglecting any potential other oxidants) against those measured (i) by LIF (assuming RO₂=HO₂) and (ii) measured by PERCA should be included. Such a

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figure would be of great assistance to the reader for appreciating the need for additional oxidants. It is extremely difficult to judge the differences from the plots shown in the paper.

5. There is too little information given in the paper for assessing the quality of the LIF and PERCA measurements. How were the instruments calibrated during the cruise? Was the same calibration source used or have the calibration sources been compared? The discussion about artefacts in BLC and the PERCA measurement (3.3 and 3.4) mainly repeats well known issues that have partially been described earlier in the paper. I think an important point to discuss (with appropriate figures!) is the difference in “ROx” concentrations determined by PSS and PERCA. This is difficult to quantify from the comparison of Fig. 4 and 7. The PERCA measurements show a clear tendency of increasing ROx concentrations during the time period showed, both at night and during daytime. This may point to an artefact, possibly related to contamination of the inlet. Has this been investigated? In this context, it would be again interesting to see the coincident NO and NO₂ measurements in the time series.

Technical comments:

1. I would suggest to combining Figs. 4, 6, and 7 in order to make the comparison easier for the reader. In addition, a scatter plot of PSS derived ROx versus PERCA and LIF should be included.
2. There is a lot of redundancy in the experimental sections that should be removed. Simple and well established procedures, such as GPT, do not need lengthy explanations. The same holds for error propagation, which is textbook knowledge and doesn't merit showing lengthy equations. The space should be used for more important details of the data quality as noted above and for expanding the discussion.
3. The paragraph on Page 7069, starting at line 4 is not clear and remains inconclusive. It should be reworded and substantiated.

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4. I would think that “diel” should be replaced by “diurnal”.

Interactive comment on Atmos. Chem. Phys. Discuss., 11, 7045, 2011.

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